

# Thermalization Breakdown and Conductivity Improvement within the Interacting Dynamic Disorder Model

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Based on the framework of Kubo formulism, we develop the minimally entangled typical thermal state algorithm to study the temperature and time dependence of current-current correlation function in one-dimensional spinless fermion model, taking into account both the electron-electron (e-e) intersite interaction and the dynamic disorder induced by classical phonons. Without e-e interaction, the numerical results, showing an exponential decay of the time dependent correlation, could be precisely compared with that from the analytical derivation, namely, from the generalized Langevin equation. More importantly, when a strong enough e-e interaction is presence, we find a long-time correlation in the regime of small dynamic disorder, indicating the breakdown of thermal relaxation, which is a typical many-body effect. On the basis of this finding, we show that it might be applied to understand the metalliclike charge transport and the abnormal improvement of the conductivity with respect to the redoping experiment in  $K_3C_{60}$ , an organic superconducting material.

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Recent progresses of organic superconducting materials, such as potassium-doped picene,[1, 2] phenanthrene,[3] coronene,[4] and dibenzpentacene,[5] has opened a new research subfield in organic electronics, due to the following two critical points: The electron-intramolecular-vibration interaction,[6, 7] together with the intercalant and intermolecular phonons,[8–10] are substantially responsible to the superconductivity; The materials are typical strongly-correlated electron systems.[10–12] Both the two statements are from first-principle calculations, and an in-depth model computation is not found. On the other hand, even under room temperature, once doped with alkali metal, those originally semiconducting materials become to behave metalliclike conductivity.[1, 13, 14] Intuitively, the doping of alkali metal has modified the  $\pi$ -electron structure of the organic molecules,[1] and the electron-electron (e-e) Coulomb interaction becomes to improve the conductivity. But in a classical manner, the e-e interaction always plays a negative role (blocking) in the charge transport.[15] This contradiction implies that, a completely quantum description should be addressed for this subject, which is the main motivation of this work.

Beyond (semi-)classical treatment, there have been many quantum theories for the transport in organic solids.[16–23, 25] Most of the works paid attention to the subjects, such as the unified bandlike and hopping mobility,[16–19] the static and dynamic disorder,[20–23] and the mixed quantum and classical problems.[25] In particular, the dynamic disorder model,[20] based upon the one-dimensional Holstein-Peierls Hamiltonian with both intra- and inter-molecular phonons treated classically, was extensively used to comprehensively understand the behavior of transport in organic crystals.

Originally, one used the Ehrenfest method to simulate the diffusion behavior of an initially localized electron wavepacket[20–22] and successfully given the basic carrier's bandlike mobility.[21] However, as those works were mainly working within one-particle picture, they make no sense of the fluctuation of the particle number, so that the dynamical response could not be evaluated. To fix this problem, the Kubo formulism was taken into account, in which the mobility is directly related to the current-current correlation function.[18, 23] It was obtained that, both bandlike and hopping transport could be described, that is, the localization length decreased quickly when the electron-phonon (e-p) coupling increases.[23] At the mean time, the e-e interaction is also studied on the mean field level.[19] In addition, the 1D Holstein model was also applied to study the organic superconductivity, since the e-p coupling is recognized to be mostly relevant.[26] In all, it seems to say that, one can just straightforwardly follow this line to study the e-e correlation more comprehensively, which should be the essential character of organic superconducting materials. Yet, as we will show in this Letter, the breakdown of thermalization[27–29] induced by the e-e correlation makes the problem quite novel.

The density matrix renormalization group (DMRG), a well-known numerical method, is one of the most powerful methods to deal with the one-dimensional strongly-correlated systems.[30] In the last decade, lots of effort have been put into extending the method to finite-temperature problems.[31–35] Advantages from White, who is the inventor of DMRG, are made by introducing the language of matrix product state and quantum Monte Carlo method, and a so-called minimally entangled typical thermal state (METTS) algorithm was

established.[35] This new method is highly efficient to calculate the thermal quantities of the system of one-dimensional spin (and thus spinless fermion) lattices, especially under high temperature. Furthermore, if the imaginary-time evolution operators in METTS algorithm are replaced by its real-time counterpart, which is quite straightforward, the method is then applicable for both temperature and time dependent problems. This means it finally becomes possible to study the thermodynamics of an organic electronic systems, such as Kubo formula and time-dependent current-current correlation, with both e-p and e-e interaction presence.

The model we are dealing with is a one-dimensional spinless model with near-neighboring e-e interactions, and the Holstein e-p coupling, which is treated classically, is also taken into account to act as a dynamic disorder. The Hamiltonian writes,

$$H = H_{\text{el}} + H_{\text{ph}}. \quad (1)$$

The electronic part is

$$H_{\text{el}} = -t_0 \sum_j (c_{j+1}^\dagger c_j + \text{h.c.}) + g \sum_j u_j \hat{n}_j + V \sum_j \hat{n}_j \hat{n}_{j+1}, \quad (2)$$

where  $c_j^\dagger(c_j)$  creates (annihilates) an electron on the  $j$ -th site,  $u_j$  the displacement of the  $j$ -th site,  $\hat{n}_j(\equiv c_j^\dagger c_j)$  the number operator of the electron,  $t_0$  the transfer integral,  $g$  the e-p coupling constant, and  $V$  the intersite e-e interaction. The phonon part of Hamiltonian (1) is described as

$$H_{\text{ph}} = \frac{K}{2} \sum_j u_j^2 + \frac{M}{2} \sum_j \dot{u}_j^2, \quad (3)$$

where  $K$  is the elastic constant between neighbor sites, and  $M$  the mass of a site. All the parameters in the model could be determined by first-principle calculations. For example, the intermolecular transfer integral  $t_0$  in doped corene is around 30meV,[6] and the characteristic phonon frequency in doped picene is around 18meV.[8] But in this work, we will take the dimensionless parameters, that is,  $t, K$  and  $M$  are all set to unity, such that the frequency of phonons is  $\omega = \sqrt{K/M} = 1$ .  $g$  and  $V$  will be the main adjustable parameters, and the main results are calculated in an open chain with 60 sites. To diminish the influence of open boundary condition, we have made the  $t_0$  exponential decay on several bonds near the boundary. Actually, the 1D spinless fermion model with e-p coupling has been long-termly studied to understand the superconductivity in doped fullerenes.[26] It was found that, the phase transition from Luttinger liquid phase to charge density wave occurs around  $g = 2t_0$  when  $t \geq 1$ . This critical phenomenon is also found in our

calculations, but the main physical results in this work are within the Luttinger liquid phase.

Based on the Hamiltonian, we are going to calculate the zero-frequency Kubo formula[36] defined as

$$\sigma = \frac{1}{k_B T} \int_0^\infty dt \langle \hat{I}(t) \hat{I}(0) \rangle, \quad (4)$$

where  $\sigma$  is the conductivity,  $T$  the temperature,  $\hat{I}(t) (\equiv e^{iHt/\hbar} \hat{I} e^{-iHt/\hbar})$  the current operator, and  $\langle \hat{A} \rangle$  the thermal average defined as  $\langle \hat{A} \rangle = \text{Tr}(e^{-H/k_B T} \hat{A})/\mathcal{Z}$  with  $\mathcal{Z}$  the partition function. Herein, to define the current operator  $\hat{I}$ , one should first define the polarization operator  $\hat{P}$  of the center of mass of the electrons, namely,

$$\hat{P} = e \sum_j R_j c_j^\dagger c_j, \quad (5)$$

with  $e$  the charge of electron and  $R_j$  the position of each site. Then  $\hat{I}$  could be defined by

$$\hat{I} = \frac{d\hat{P}}{dt} = \frac{1}{i\hbar} [\hat{P}, H] = -\frac{eat_0}{i\hbar} \sum_j (c_j^\dagger c_{j+1} - \text{h.c.}), \quad (6)$$

with  $a$  the lattice constant.

The current-current correlation function in the Kubo formula (4) is both time and temperature dependent. In order to evaluate it, we apply the METTS algorithm combined with time-dependent DMRG method (tDMRG),[37] whose basic procedure is as follows. Firstly, one initializes a configuration of the occupation of each site arbitrarily and then produces a so-called classical product state (CPS) as

$$|n\rangle = |n_1, n_2, \dots, n_j, \dots\rangle, \quad (7)$$

with  $|n_j\rangle$  the local basis on site  $j$ . Secondly, the imaginary-time evolution operator is acting on the CPS, namely,

$$|\phi_n\rangle = P(n)^{-1/2} e^{-\beta H/2} |n\rangle, \quad (8)$$

where  $|\phi_n\rangle$  is the so-called typical thermal state,  $P(n)(\equiv \langle n | e^{-\beta H} | n \rangle)$  the statistical probability of the state  $|n\rangle$  in the ensemble, and  $\beta$  the inverse of  $k_B T$ . In a Monte Carlo manner, the above steps are iterated, and then we get lots of (but still much fewer than the total number of state)  $|\phi_n\rangle$  samplings in hand. Based on these samplings, we calculate the expectation of any operator  $A$  as

$$\langle A \rangle = \frac{1}{\mathcal{Z}} \sum_n P(n) \langle \phi_n | A | \phi_n \rangle. \quad (9)$$

Obviously, when the number of site becomes large, the Hilbert space is enlarged drastically. Hence, one should follow the standard procedure of tDMRG, that is, the evolution operator must be decomposed onto individual bonds, and the state must be truncated while scanning

as the usual procedure in DMRG method. Meanwhile, in White's treatment, to ensure the ergodic hypothesis, one should choose another CPS by collapsing  $|\phi_n\rangle$  to (the arbitrary basis of) each site and iterate the above steps for sufficient times.

Once the thermal equilibrium is reached, that is, the typical thermal states  $|\phi_n(0)\rangle$  in the equilibrium are obtained, one can easily calculate the time evolution by changing the evolution operator with imaginary time in (8) to real time. For the aim of the present work, we are focusing on computing the time dependent current-current correlation function in Kubo formula, i.e.,  $\langle\phi_n(0)|e^{iHt/\hbar}\hat{I}e^{-iHt/\hbar}\hat{I}|\phi_n(0)\rangle$ . Hence, one should first make the current operator  $\hat{I}$  acting onto  $|\phi_n(0)\rangle$ , and then calculate the time evolution of the obtained state. At each time step  $t$ , one again act  $\hat{I}$  on the new state and calculate its overlap with the state  $e^{-iHt/\hbar}|\phi_n(0)\rangle$ . Since  $\hat{I}$  could be decomposed onto each bond of the lattice, naively, one can just act it on the individual bond in each scanning step and sum up the targeting states. But this idea is quite inefficient for tDMRG, because we need to target too many states. Our treatment is on the basis of assumption of translating invariance, namely, at the initial moment, we only act the current operator on the central bond of  $|\phi_n(0)\rangle$ , which should be the most precise bond in the approximation of tDMRG. Based on this simplicity, only two states  $|\phi_n(0)\rangle$  and  $\hat{I}_c|\phi_n(0)\rangle$  (with  $\hat{I}_c$  the current operator on the central bond) are necessary to be targeted, which makes the procedure much more efficient.

Up to now, the remaining thing is to treat the phonon part of the system. We follow the usual procedure of Ehrenfest method, which is the standard method for calculating the time evolution of mixed classical-quantum systems. That is, we first choose an initial configuration of  $\{u_j\}$  and  $\{\dot{u}_j\}$  from the Gaussian distribution with variance  $k_B T/K$  and  $k_B T/M$ , say the equilibrium distribution of vibrations. This configuration could be substituted into the Hamiltonian of electron part, and one follows the common procedure to calculate the Hellman-Feynman force that electrons act on the sites, such that, the influence of phonon comes into the theory.

Here, we need to say that, since the current operator  $\hat{I}$  does not change the total number of electron and the spin degree of freedom is ignored, the precision of the present numerical calculation should be at least in the same order with the previous tDMRG works of us in the Hubbard chain and the conjugated polymer.[38] However, the evolution is now for the typical thermal states rather than the ground state. Together with the numerical errors from the Ehrenfest method for the phonon part, the accumulation of error is very fast. Even if we decrease the number of truncated states in METTS, it seems no significant improvement is obtained, so that more efforts should be devoted to the method itself. But still, within short time scale, many interesting results

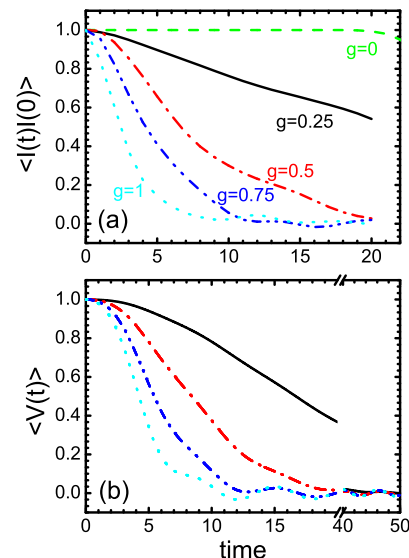


FIG. 1: (a) The current-current correlation function (in the unit of  $(eat_0)^2/2N_c\hbar^2$ ) versus time (in the unit of  $\hbar/t_0$ ) with various e-p coupling. (b) The averaged velocity from the generalized Langevin equation.[39] The relaxation time for  $g = 0.25$  is around 50.

have been found.

In Fig. 1(a), we first show the results of current-current correlation function without e-e interaction under  $k_B T = 2$ . For  $g = 0$ , i.e., the disorder is absent, the electron is completely free. One can easily prove that, in this case,  $\hat{I}$  commutes with  $H$ , so the correlation function is unchanged with time. As we see that, the curve remains a constant up to  $t = 20$ , but due to the accumulation of numerical error, the curve goes down quickly after that point. Hence,  $t = 20$  should be a point of justification that, before it the numerical results are credible. In addition, we find that, following  $g$  increasing, the decay of the correlation becomes much faster, and above  $g = 2$  (not shown), the correlation acts nearly a sudden quenching, which means it is within an insulating phase.

To check the correctness of the present numerical algorithm, a method beyond the framework of Monte Carlo sampling is needed. Here, we adopt the generalized Langevin equation (GLE) to calculate the time dependence of thermal averaged velocity.[39] Although not exactly the same, the oscillation and decay of the averaged velocity are expected to follow the similar trajectory with that of current-current correlation function. To compare with the METTS results, in Fig. 1(b), we show the result of  $V(t)$  from GLE with the same  $g$ 's, respectively. Qualitatively, both the wavy and decay shape agree with the result from METTS. And more importantly, when  $g$  decreases by the same times, the decay velocity shows very close value, which could not be adjusted by any parameters. These results not only allow us to doubly check the correctness of the numerical algorithm, but also pro-

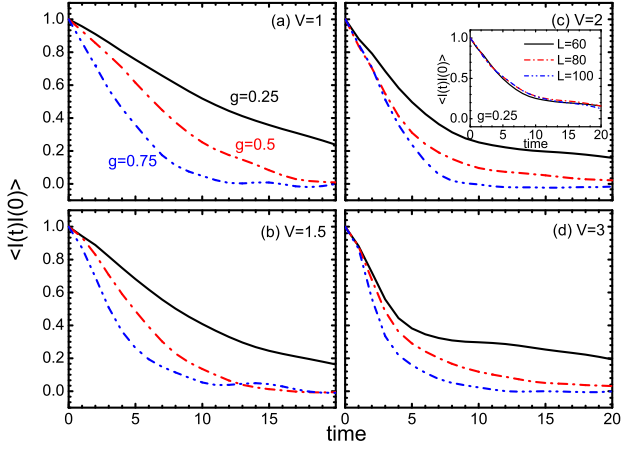


FIG. 2: Time dependence of current-current correlation function for various  $g$  and  $V$ . Inset of (c) shows the little influence of the finite length scale.

vide more information that METTS can not give. For example, the GLE result shows the relaxation behavior for all  $g$  after a long time evolution with the relaxation time is around 50. This complement is very important to understand the following results.

Now, we are on the stage to show the influence of e-e interaction. In Fig. 2, we show the time dependent correlation for various  $V$  and  $g$ . Compared with  $V = 0$  case, when  $g$  is larger than 0.5, the velocity of decay increases with increasing  $V$ . This is easy to understand, since the system tend to the insulating phase. But quite interestingly, as one can see from (a) to (d) that, when  $g = 0.25$ , although the velocity of decay still tends to increase in the very beginning of evolution, it seems that the curve does not vanish but relax to a finite value (around 0.15) after a long time. Of course, one may argue that, our numerical method can not show the result of long-time evolution, but we can still estimate from the present result that, the relaxation time for  $V = 2$  should be at least much longer than that in uncorrelated system ( $\gg 50$ ). Meanwhile, to exclude the influence of the chain length, in the inset of Fig. 2(c), we show the result for different site number, and obviously, they are almost the same. Hence, this long-time memory effect of correlation function is the main finding of this work. It is non-asymptotic from the uncorrelated system, since it implies the thermalization breakdown induced by the e-e interaction.[27] Actually, the breakdown of thermal relaxation in fermion systems was widely studied very recently.[28, 29] That is, when the main-body correlation enters into the low-dimensional fermion system, the relaxation to thermal equilibrium should be strongly related to the initial state, due to the complex entanglement between equilibrium and nonequilibrium correlations in correlated systems.[28] The present results agree with these works and add more information on this sub-

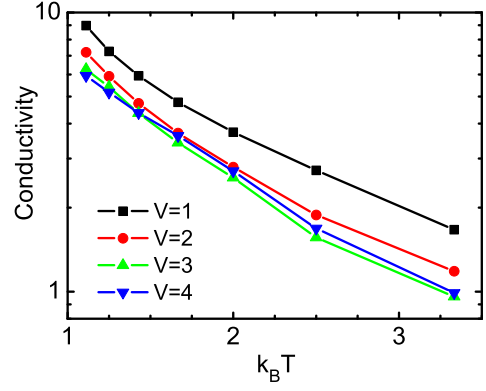


FIG. 3: Temperature dependence of conductivity (in the unit of  $t_0(ea)^2/2h$ ) calculated from Kubo formula for various  $V$ .

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Intuitively, since the conductivity is related to the integral of current-current correlation function within the framework of Kubo formula, the long-time memory effect found above should contribute a lot to the conductivity and improve it. This statement obviously contradicts to the conventional point of view, as the Coulomb repulsion in the material with small disorder is always recognized to act as a blocking and thus will lead to the reduction of conductivity.[15] Whereas, the improvement of conductivity was indeed found in  $K_3C_{60}$  by redoping of alkali metals, as shown in [13]. The redoping process is, in our opinion, to increase the concentration of alkali metallic atoms and thus the Coulomb interaction among them. The improvement of conductivity is surprising and full of meaning, since it is closely related to the increase of  $T_c$  of these organic superconducting materials.[13] On the basis of our present finding of the memory effect, we could then provide a possible explanation on the experiment. In Fig. 3, we show the main results of the temperature dependence of conductivity. Here, due to the limit of numerical method, the time integral in the Kubo formula (4) is only within  $t < 20$ . This is equivalent to considering an additional static disorder  $1/\tau_s$ , i.e., the time integral in Kubo formula becomes[18]

$$\int dt \rightarrow \int dt e^{-(t/\tau_s)^2}. \quad (10)$$

It is found that, when  $V < 2$ , the result is quite the same with the bandlike behavior in common dynamic disorder model.[20] When  $V \geq 2$ , the relationship between conductivity and temperature becomes to metalliclike, namely,  $\sigma \sim 1/T$ . More importantly, the curve of conductivity stops decreasing but becomes close with each other. Even in the high temperature regime and  $V = 4$ , we find a cross of the curves and improvement of the conductivity, which are consistent with that of doped and annealed cases as shown in the Fig. 3 of [13]. Therefore, we could now conclude that, the thermalization break-

down induced by the e-e interaction matters in the charge transport of alkali-metal-doped organic materials.

Finally, we would like to briefly discuss the superconductivity in organic solids. Different from their inorganic counterparts, organic materials have much more diverse vibrational modes, such that the decoherence process could easily kill the phase correlation of the electron wavefunctions and thus the tendency of superconductivity. To avoid this effect, the high frequency part of the phonons, which is the main source of decoherence,[24, 40] must be largely suppressed. The present work provides a possibility, that is, the long-time memory of electric current induced by e-e interaction should be a shield against the decoherence and contribution to the conduction of these materials.

In summary, we have used the METTS algorithm to calculate the temperature and time dependent current-current correlation function in a one-dimensional spinless model with both e-e and e-p interaction taken into account. Via the comparison with analytic results, we state that, this very new method works well within a short time scale. Then we study the influence of e-e interaction and find a long-time memory effect, say, the thermalization breakdown of the system. Based on this finding, we calculate the temperature dependent mobility and show that, following the increase of e-e interaction, the mobility will behave a slight enhancement, which was also found in the experiment.

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# Thermalization Breakdown and Conductivity Improvement within the Interacting Dynamic Disorder Model: Supplementary Material

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In order to make sense of the long-time behavior for  $V = 0$ , we adopt the generalized Langevin equation (GLE).<sup>1,2</sup> The basic idea is to separate the electronic Hamiltonian into the center-of-mass and relative part, namely,

$$H = \frac{\hat{P}^2}{2M_e} + \sum_k \epsilon_k \tilde{c}_k^\dagger \tilde{c}_k + g \sum_q e^{iq\hat{R}} u_q \tilde{\rho}_q, \quad (1)$$

where  $\hat{P}$  is the momentum of the center of mass,  $\hat{R}$  the conjugate variable of  $\hat{P}$ ,  $M_e = Nm_e$  with  $N$  the number of electron and  $m_e$  the mass of a single electron,  $\epsilon_k$  the energy with  $k$  the wave vector of "relative" electrons,  $\tilde{c}_k^\dagger$  ( $\tilde{c}_k$ ) the creation (annihilation) operator of relative electrons with  $\tilde{\rho}_q (\equiv \sum_k \tilde{c}_{k+q}^\dagger \tilde{c}_k)$  the corresponding density operator, and  $q$  the wave number. It could be demonstrated that, the operators of center-of-mass and relative part commute with each other.<sup>3</sup> Meanwhile, only the contribution of small  $q$  is assumed to be dominant, so that the relative part acts as a source of fluctuations for the center of mass via the assistance of phonons.

Within this Hamiltonian, we are going to evaluate the derivative of  $\hat{V} (\equiv \hat{P}/M_e)$  at time  $t$ . In the interaction picture, it could be written as  $(\hbar = 1)$ <sup>1</sup>

$$\frac{d\hat{V}}{dt} = \hat{F}(t) - \int_0^t dt' [\hat{F}(t'), H_{ep}(t')], \quad (2)$$

where  $H_{ep}$  is the last term of (1), and  $\hat{F}(t)$  is the fluctuating force operator defined as

$$\hat{F}(t) = -ig \sum_{q'} e^{iq'\hat{R}} q' u_{q'} \tilde{\rho}_{q'}. \quad (3)$$

Since  $q$  is small, we can expand the exponential term to the linear order, that is,  $\exp(iq\hat{R}) = 1 + iq\hat{R}$ . Then Eq. (2) becomes

$$\frac{d\hat{V}}{dt} = \hat{F}(t) - \int_0^t dt' g^2 (\hat{R}(t) + \hat{R}(t')) \sum_q q^2 u_q^2(t, t') \cdot [\tilde{\rho}_q(t), \tilde{\rho}_q(t')], \quad (4)$$

where the zero-order term is absorbed into the fluctuating force, and the high-order term of  $q$  is neglected.  $q'$  is equal to  $q$  in order to ensure the conservation of the total momentum.

Following the Ehrenfest theorem, the dynamics of classical phonons could be treated as  $u_q^2(t, t') \simeq k_B T \sin(\omega(t - t'))/K$  with  $\omega$  its frequency and  $K$  the elastic constant.<sup>2</sup> The last term, say  $[\tilde{\rho}_q(t), \tilde{\rho}_q(t')]$ , behaves as a relaxation term and is significant when  $t = t'$ . It is not easy to derive an explicit expression for this term, but it could be estimated to be  $\sim n/q^2$  with  $n$  the density of electron.<sup>1</sup> In all, we then define a dimensionless parameter  $\xi$ , which denotes the thermal average of the summation, i.e.,  $\langle \sum_q q^2 u_q^2(t, t') \cdot [\tilde{\rho}_q(t), \tilde{\rho}_q(t')] \rangle = \xi \sin(\omega(t - t'))$ . Actually,  $\xi$  equals to the intensity of the fluctuating force and is proportional to  $k_B T$ .<sup>1,2</sup> Finally, by taking the thermal average and using integration by parts, Eq. (2) becomes the GLE as

$$\frac{d\hat{V}}{dt} = \hat{F}(t) - \xi g^2 [2\hat{R}(t) - \int_0^t dt' \cos(\omega(t - t')) \hat{V}(t')], \quad (5)$$

where we have used  $\hat{V}(t) = d\hat{R}(t)/dt$ , and the cosine term is absorbed into the fluctuating force. Here  $\xi$  is an adjustable parameter, and when it is sufficiently small,  $\hat{R}(t) \simeq \hat{V}(t)t$ . To compare with the numerical results, we will set  $\xi$  to be 0.04. Then we take the thermal average for all the quantities and make  $\langle \hat{F} \rangle$  vanishing. The numerical integration is now available for  $V(t)$  when we consider  $V(0) = 1$  as the initial condition.

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